Preface

Introduction and Motivation

Physical properties of materials and their constituents are interrelated. Though the basic structural unit involved also plays a role in deciding the properties, this can be manipulated to a certain extent, by carefully selecting the basic ingredients or by varying the composition. In order to tailor the properties of the materials according to the need, the relationship between the properties and the structure has to be established.

Glasses, due to their inherent disorder, don't have the privilege of using symmetry as enjoyed by their crystalline counterparts. Given their components and composition there is no immediate and easy way of predicting all the observed properties of glasses. This is not considering computer simulations and DFT calculations. Hence we go back to play with nature, i.e., do experiments.

Technological applications like LASERs, optic fibers, photosensitive semiconducting thin films, solid state batteries for energy storage etc. have greatly increased the interest in the fundamental properties of disordered materials. Large coefficient of linear expansion of germanate glasses is made use in glass-to-metal seals for ultra high vacuum. More over, many germanate based glasses with specially tailored dispersion properties have been developed. GeO_2 based glasses are in fibre optics in the IR region of 1.5 to 1.8 microns. Borate glasses are resistant to thermal and chemical attack. They lower the melting temperature of glasses thus facilitating large scale production.

Both borates and germanates have been worked upon extensively. Alkali boro germanate systems are interesting inherently. Borates and Germanates both are glass formers by themselves. The continuous random network formed by this base glass is modified by the presence of alkali ions. It is interesting to see to what extent the alkali ions can maintain the local charge neutrality in their neighborhood by creating non bridging oxygen atoms and how the presence of two formers is stabilizing the glass matrix.

Present Work

This thesis work is an attempt to understand the structure of alkali borogermanate glasses $25R_2O$-$25GeO_2$-$(50-x)B_2O_3$-xNd_2O_3:(R=Li, Na, K and Rb; x=0,0.5). A variety of experimental techniques are available to give a good insight of the structure of glass systems. In this thesis, we have carried out

- Optical studies at room temperature to probe the environment of RE ion
- AC conductivity at high temperature to probe the alkali ion dynamics
- ^{11}B MASS NMR of doped systems at room temperature to probe the Boron sites
- Raman and Mid-IR experiments at room temperature to probe the various structural groups

to get a comprehensive understanding of the structure of these glasses. To facilitate the analysis of the data and discussion of the results from these experiments, the thesis is divided in to four chapters excluding the introduction as categorized above and is presented accordingly.

The second chapter begins with the preparation of the glass samples and their characterization. We have used Differential Scanning Calorimetry (DSC), powder XRD and elemental analysis using ICP-OES for characterizing the sample. We have also measured the density and refractive index of the glasses under study. After this section, we describe the results from Optical Absorption and Photoluminescence studies. A brief

description of Judd-Ofelt (JO) theory used for the analysis of the results is given. We have calculated the optical parameters and JO parameters and the energy levels of Nd ions in the glass matrix based on absorption studies using program written in Matlab. The procedure to calculate these parameters and their relevance in estimating the important quantities like radiative transfers, branching ratios are discussed. The effect of variation of the alkali ions on these properties is also discussed.

In the third chapter, we have investigated AC conductivity in these glasses. These experiments are carried out both as a function of frequency (40 Hz - 15 MHz) and temperature (220 °C – 500 °C) using a home made portable furnace with a temperature controller. The cable compensation using open and short standards were done at the high temperature end. The data has been analyzed in Electric modulus (M^*) formalism using Kohlrausch William Watts (KWW) function. The other basic models used in the literature like Debye, Cole-Cole, Cole Davidson and Havriliak Negami are briefly discussed. The frequency dependence of conductivity in these systems has been ascribed to the hopping motion of the alkali ions. Non-symmetric nature of the imaginary part of M^* shows an evidence of non-exponential relaxation. Activation energies were estimated from the temperature variation of the τ_{KWW} and $\sigma_{DC.}$ The fit parameters β_{KWW} and τ_{KWW} shows interesting behavior. β_{KWW} in LGBNd and NGBNd show an initial increase with increasing temperature reaching a value of 1, while a contrasting behavior is observed in KGBNd and RGBNd. Barton-Nakajima-Namikawa (BNN) plot of the present study gives a value of 0.67 and 0.7 for the slope parameter p for doped and un-doped samples respectively. BNN plot is used to correlate the ac and dc conductivities in the sample.

The deviation of the slope parameter from unity may be an indication of different charge carriers for ac and dc transport.

Fourth Chapter describes the room temperature ^{11}B MASS NMR studies in Nd doped glass system. The relevant theory of Zeeman, Dipolar, Quadrupolar and Chemical shift interactions are discussed briefly before the results. The principle used in obtaining high resolution NMR in solids by means Sample spinning is also described. NMR line shape for the central transition ($1/2 \leftrightarrow -1/2$) of I=3/2 nuclei (^{11}B) was simulated in Mathematica and fitting was tried in Matlab. Using this background we have analyzed the line shape. In the next part, the results of ^{11}B MASS NMR experiments of doped glasses carried out using Bruker DSX300 at 96.3MHz are presented. The fraction of contribution from four and three co-ordinated ^{11}B to NMR line-shape were identified and calculated. The results show unambiguously the presence of two 3 coordinated ^{11}B sites which were differentiated on the basis of the quadrupolar parameters.

In the last chapter we discuss the results of Raman and Mid-IR investigations carried out in these glasses at room temperature. These two important techniques are well established in identifying the structural groups in glass systems. Raman bands observed in the range 200 cm^{-1} to 1600 cm^{-1} in these glasses are deconvoluted using gaussian peaks and they have been assigned to various modes of possible structural groups. Two broad MIR absorption bands were observed between 600cm^{-1} - 1600cm^{-1} in both doped and un-doped glasses. Each band was resolved into gaussian peaks. The band shifts and the changes in the intensities are ascribed to the effects of variation of alkali, as the presence of GeO_2 (up to 25mol%) is known not to affect the borate bands as it is a former by itself.